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THE EFFECT OF WATER ADDITION ON PHYSICOCHEMICAL PROPERTIES OF ELECTROCHEMICAL SYSTEMS BASED ON DEEP EUTECTIC SOLVENTS

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We investigated the effect of water addition on physicochemical properties of ionic liquids containing (i) chromium chloride, choline chloride and water in the molar ratio of 1:0.5:*x*, and (ii) choline chloride, ethylene glycol, nickel chloride and water in the molar ratio of 1:2:1:*x*, (*x* = 6, 9, 12, 15 or 18) for the temperatures between 25 and 80 °C. An increase in the water content resulted in decreasing density, viscosity and surface tension and increasing conductivity. The obtained results were interpreted in terms of hole theory. The introduction of water was stated to have a beneficial effect on the electrodeposition of chromium and nickel coatings.

Electrochemical systems based on deep eutectic solvents (DESs) are now considered as a promising alternative to common aqueous electrolytes [1]. DESs have an ionic character and may be considered as a new class of ionic liquid analogues; they consist of a eutectic mixture of compounds having a melting point significantly lower than that of either individual component [1, 2]. Commonly, DESs consist of quaternary ammonium salt such as choline chloride (2-hydroxy-ethyl-trimethyl ammonium chloride) and a hydrogen bond donor species such as amides, glycols or carboxylic acids). Similarly to usual ionic liquids, DESs have relatively wide potential electrochemical window, the high solubility of metal salts, negligible vapor pressures and high conductivity compared to non-aqueous solvents [1].

Electrodeposition of various metals and alloys using DESs have been received significant attention as deep eutectic solvents are cheap, easy to synthesize, easily biodegradable and not harmful for the environment compared to most other ionic liquids [1, 3].

It is known that electrodeposition processes from DESs based systems may be sufficiently improved by the introduction of water additives into electroplating baths [4, 5]. In this context, water molecules added to DESs can be considered as a special hydrogen bond donor. This study was aimed to ascertain the effects of extra water addition on the main physicochemical properties of ionic liquids containing $CrCl_3 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$ and on the electrodeposition of chromium and nickel films.

Research Methodology

Choline chloride was recrystallized from isopropanol then filtered and dried under vacuum. Chromium(III) and nickel(II) chlorides were used as they were received. The ionic liquids were prepared by mixing choline chloride and $CrCl_3 \cdot 6H_2O$ or $NiCl_2 \cdot 6H_2O$ in a thermostatic heater at 70 °C by stirring until a homogenous liquids had formed. Then a required amount of extra bidistillate water was added to the mixture and stirred at the same elevated temperature in order to obtain a homogenous liquid mixture. Density measurements were performed using a glass specific gravity bottle. The surface tension was determined by means of Wilhelmy plate method. Viscosity measurements were performed with a glass Ubbelohde type viscometer. Conductivity measurements were performed by means of usual ac Wheatstone bridge.

Electrodeposition experiments were carried out in a thermostated glass cell. Chromium and nickel were deposited at a constant value of current density on the disc electrode of copper foil fixed in a plastic holder. Platinum gauze and nickel plate were used as anodes without separation of anodic and cathodic compartments for Cr and Ni plating, respectively.

Results and Discussion

Chromium(III)-containing systems

The effect of water addition on physicochemical properties of liquid mixtures was investigated for the systems containing $CrCl_3$, choline chloride and water in the molar ratio of 1:0.5:x (where x = 6, 9, 12, 15 or 18). As expected, density, surface tension and viscosity decrease with increasing temperature and water content in the liquid mixtures. On the contrary, conductivity increases with temperature and water content. Some of the obtained results are shown in Figures 1 and 2.

It is well-known that hole theory can be used to explain the mobility of particles in deep eutectic solvents. According to this concept [1], ionic liquids (including DESs) contain empty spaces arising from thermally generated fluctuations in local density. The vacancies are of a random size and position; they are in constant motion. An ion can only move through an ionic liquid if it is adjacent to a hole of equal or greater size.

The average hole size (r) in an ionic liquid is given by the following relationship [1]

$$4\pi\langle r^2\rangle = 3.5\frac{kT}{\gamma}$$

where γ is the surface tension, k is the Boltzmann constant and T is the absolute temperature.

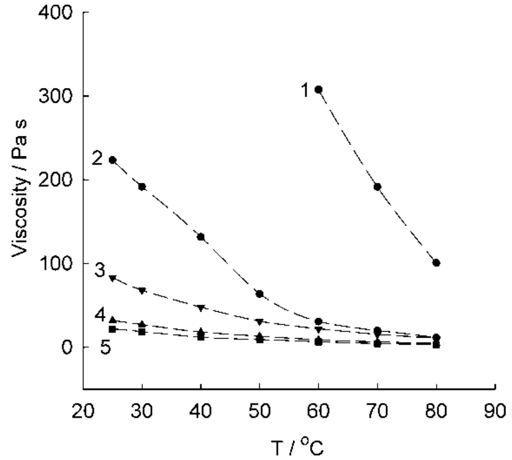

Fig. 1. *Viscosity of $2CrCl_3$ + ChCl + xH_2O mixtures as a function of temperature.*
x = 6 (1), 9 (2), 12 (3), 15 (4), 18 (5)

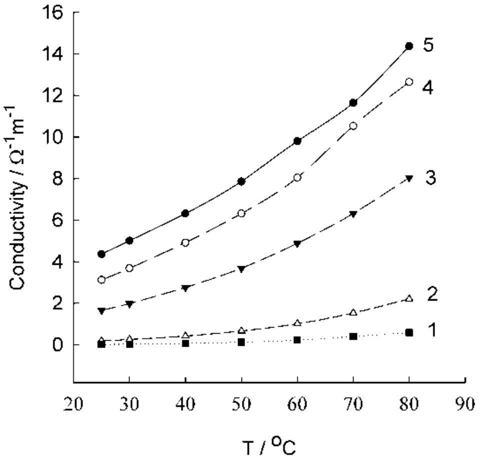

Fig. 2. *Conductivity of $2CrCl_3$ + ChCl + xH_2O mixtures as a function of temperature.*
x = 6 (1), 9 (2), 12 (3), 15 (4), 18 (5)

The calculated average void radii for the systems under consideration are shown in Table 1. As can be seen, increasing both temperature and water content leads to an appreciable increase in average void radius. As the natural result, this will promote decreasing viscosity and increasing conductivity.

Table 1. Calculated average void radii for $2CrCl_3$ + ChCl + xH_2O mixtures

T (°C)	r (Å)				
	x = 6	x = 9	x = 12	x = 15	x = 18
25	0.732	1.254	1.287	1.315	1.509
30	0.741	1.268	1.306	1.332	1.530
40	0.765	1.304	1.343	1.374	1.583
50	0.788	1.340	1.389	1.428	1.648
60	0.811	1.383	1.437	1.481	1.714
70	0.839	1.424	1.488	1.536	1.773
80	0.866	1.482	1.550	1.602	1.832

The temperature dependences of viscosity and conductivity were processed using logarithmic form of Arrhenius equation and the corresponding values of activation energies were calculated. Both activation energy for viscous flow and activation energy for conductivity diminish with increasing water content in liquid mixtures. Lower activation energies correspond to more mobile ions within the melt. Therefore, the obtained results are in good agreement with the estimation of average hole sizes: an increase in r makes ionic motion considerably easier.

Thus, the introduction of extra water into the systems results in an appreciable improvement in some properties of liquid mixtures: a decrease in viscosity and an increase in conductivity are observed. This feature is important and favorable in terms of the possible practical application of plating baths containing DESs. However, the results of electrodeposition experiments reveal that an increase in extra water concentration leads to a decrease in current efficiency due to the acceleration of competitive hydrogen evolution reaction. Taking into account these considerations, we conclude that the chromium electroplating should be performed from liquid mixtures of $2CrCl_3$ + ChCl + xH_2O with intermediate water content (x = 9 or 12).

Nickel(II)-containing systems

The effect of water addition on the physicochemical properties of liquid mixtures was investigated for the systems containing choline chloride, ethylene glycol, nickel chloride and extra water in the molar ratio of 1:2:1:x (i.e. ethaline + $NiCl_2$ + xH_2O) where x = 6, 9, 12 or 18.

Analogous to chromium-containing ionic liquids, an increase in the water content (x) results in decreasing density, viscosity and surface tension and increasing conductivity (see Figures 3 and 4 for references).

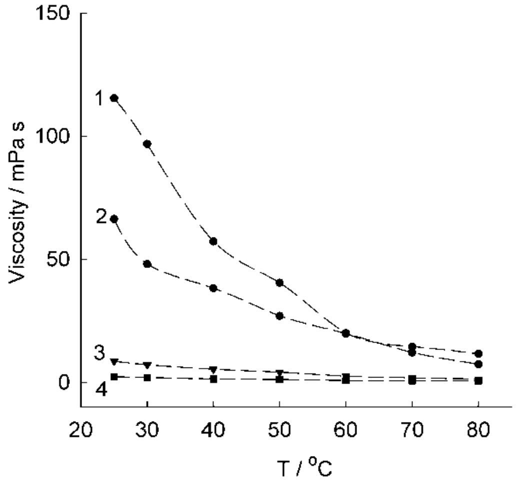

Fig. 3. *Viscosity of ethaline + $NiCl_2 \cdot xH_2O$ mixtures as a function of temperature.*
x = 6 (1), 9 (2), 12 (3), 18 (4)

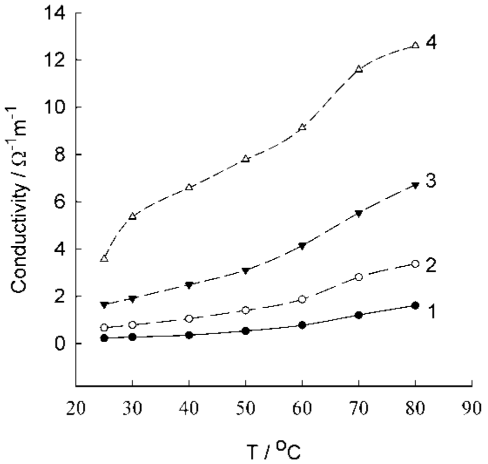

Fig. 4. *Conductivity of ethaline + $NiCl_2 \cdot xH_2O$ mixtures as a function of temperature.*
x = 6 (1), 9 (2), 12 (3), 18 (4)

The calculated average hole sizes in the liquid systems under study are summarized in Table 2, the value of r being increased with increasing both temperature and water content. This means that ionic motion becomes easier.

Nickel electrodeposition experiments showed that high-quality nanocrystalline Ni deposits can be obtained from the electroplating bath on the basis of DESs with water addition. The current efficiency of Ni electrodeposition reaction reaches 95-100%. The coatings morphology becomes finer at higher water concentrations. Our preliminary results showed that the microhardness and corrosion resistance of Ni coatings can be enhanced with an increase in water content in the plaiting bath.

Table 2. Calculated average void radii for ethaline + $NiCl_2{\cdot}xH_2O$ mixtures

T (°C)	*r* (Å)			
	x = 6	*x* = 9	*x* = 12	*x* = 18
25	1.207	1.220	1.234	1.248
30	1.223	1.236	1.251	1.265
40	1.256	1.270	1.285	1.300
50	1.289	1.295	1.314	1.336
60	1.325	1.332	1.347	1.370
70	1.356	1.372	1.393	1.406
80	1.391	1.410	1.425	1.444

Conclusions

1. The introduction of extra water into the ionic liquids containing $2CrCl_3$ + ChCl + xH_2O or ethaline + $NiCl_2{\cdot}xH_2O$ has a beneficial effect on the physicochemical properties of the plating bath: an increase in conductivity and a decrease in viscosity are observed.

2. High-quality Cr and Ni coatings with a relatively high current efficiency can be electrodeposited from the plating bath based on DESs with extra water addition.

References

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